Quantifying and Predicting Reactive Transport of Uranium in Waste Plumes: Are Colloids and Nanoparticles Important?
(Project 90171)

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Research Objectives

The Hanford Site is the DOE's largest legacy waste site, with uranium (U) from plutonium processing being a major contaminant in its subsurface. Accidental release of highly concentrated high-level wastes left large quantities of U in the vadose zone under tank farms. The U contamination has been found in groundwater beneath the tank farms, indicating U is mobile. Because excavation costs are enormous, this U will likely be left in-ground for the foreseeable future. Therefore, understanding the contamination processes and the resulting U spatial and temporary distributions and mobility in the heavily contaminated Hanford site is needed in order to forecast its future transport. The overall objective of this research is to develop an experimentally supported conceptual model of U reactive transport, during and after the tank leakage, at heavily U-contaminated areas of the Hanford vadose zone. The conceptual model will incorporate key geochemical and physical controls on the contamination process, explain the current distribution of U in the vadose zone, and guide predictions of its future mobility under the influence of natural recharge. We do not seek to predict the complex flow geometry of any specific waste plume. Instead, our work is trying to identify the hierarchy of processes relevant along U waste plume paths.

Research Progress and Implications

This report summarizes progress of the project during the past three years (2004-2006). In pursuit of our research objective, we chose to simulate the tank BX-102 /over-fill event (the largest single spilling event of U release in the country, left 8 tons of U in the vadose zone). We synthesized the Metal Waste Solution (MWS) based on the historical recipe. The MWS contained 0.11 M U(VI), 3.6 M sodium, 0.6 M carbonate, and had a pH of 10.4. The tank waste spilling event was simulated using the column plume profiling method we developed earlier (Figure 1). The synthesized MWS was injected into columns of different lengths, at 70˚C, and at varied flow rates. Flow was stopped just before the plume front reached the opposite end of the column. Then the column was sectioned and the pore liquid was extracted from each segment of the column. Temporally and spatially resolved chemical and physical properties of plume pore liquids and sediments were determined to obtain profiles of geochemical characteristics of the plumes. The main findings are summarized here.

1. Massive quantities of U-containing colloids formed within plume front pore liquids. The extracted plume liquid at plume front location contained massive quantities of colloids, including U containing colloids (Figure 2, 3).

2. Dramatic pH decrease found in plume front pore liquids. The pH decreased to as low as 6.4 at the front; 4 units lower than the pH of initial waste solution (pH 10.4), *and* two units lower than the pH of the displaced native sediment water (pH 8.4). The pH reduction at the plume front is largely responsible for colloid formation at the plume front location.
3. Large Ca^{2+} and Mg^{2+} enrichment found within plume front pore liquids. Sharp Ca^{2+} and Mg^{2+} peaks were found at the plume front liquids. As a consequence, precipitation of these supersaturated divalent cations as carbonates resulted in pH reduction at the plume front.
4. Fast U transport found within plumes. Fast U transport in the plume liquid phase was observed, with very high concentrations of U accumulated at the plume front. Uranium peak concentrations reached as high as 5.8 times of the initial U concentration in the injected waste solution. The fast transport of U most likely resulted from the formation and preferential (size exclusion) transport of U-colloids.
5. Flow rate is an important control on overall U behavior in the waste plumes. The extent of all aforementioned phenomena increase with increased flow rate. The degree of U retardation by sediments increased with reduced flow rate, showing that kinetics of sorption and precipitation controlled retardation.
6. The geochemical properties of laboratory plume profiles can be scaled up to be field-relevant when applied along appropriate flow paths (generally not 1-dimensionally). The aforementioned conclusions (1 through 5) are now well tested for plume lengths from 0.2 to 2.0 meters.

Reactive transport modeling for matching the time-dependent liquid saturation and non-reactive tracer fronts in the column experiments is in progress. Modeling of the solution pH was carried out by including various mineral precipitation and dissolution reactions, the most important of which is calcite. Calcite precipitated because of the high bicarbonate in the injection solution and because of the desorption of Ca^{+2} from cation exchange sites on the clays as a result of the elution of the high Na^{+}, which competes for exchange sites with the Ca^{+2}. The precipitation of calcite releases hydrogen ion, thus lowering the pH. The simulations predict the precipitation of minor amounts of sodium uranium carbonate, a phase identified by XRD in the columns, but only upstream of the calcite front, since the precipitation of calcite decreases bicarbonate in solution and de-stabilizes the sodium uranium carbonate. The modeling results will be soon summarized in a manuscript.

Although U geochemistry has been extensively studied, the processes of U-colloid precipitation and fast U transport within the plumes have not been previously revealed, and was not predictable using transport models that assume local equilibrium (K_d). This may explain the efficient U transport and highly variable retardation observed within the alkaline waste plumes in the field.

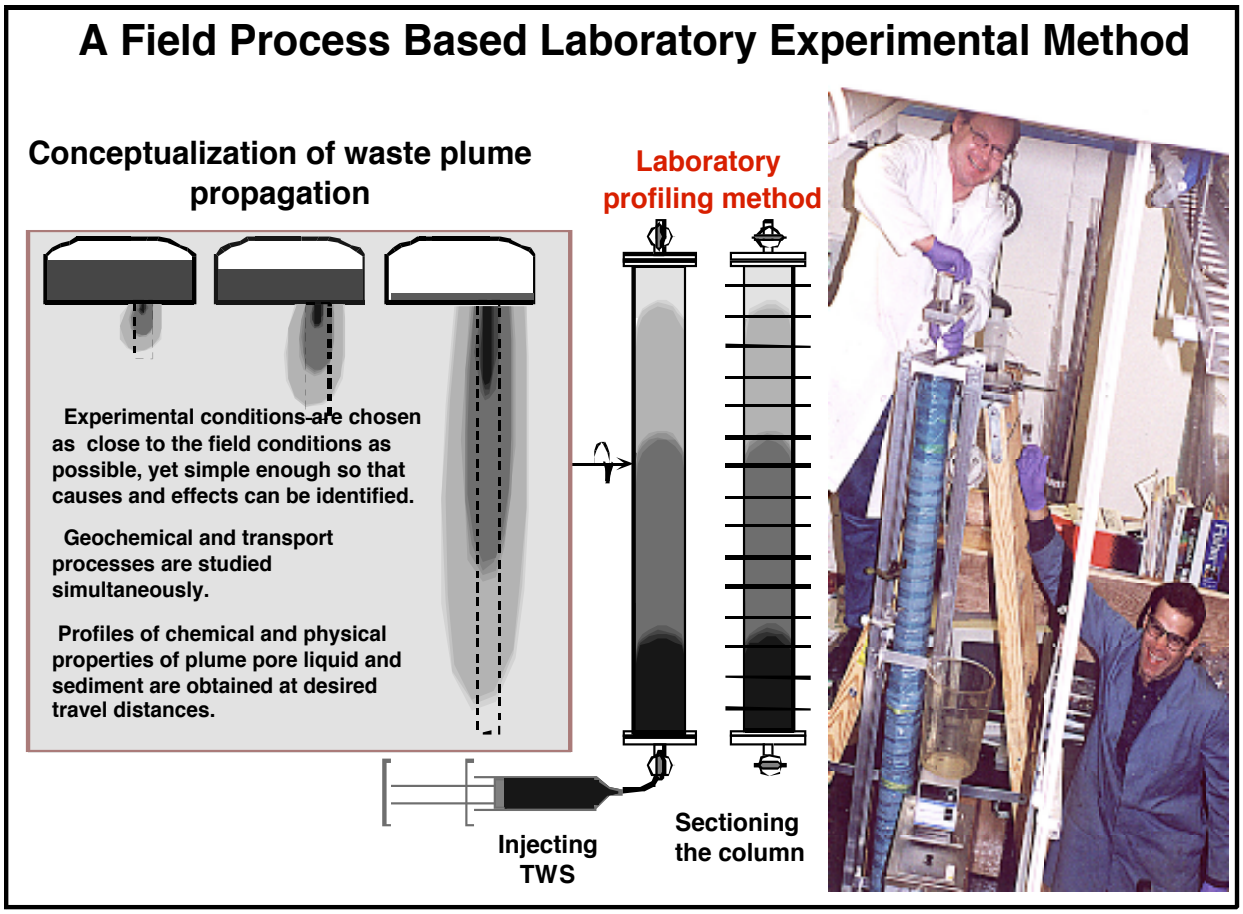

Figure 1. Laboratory column plume profiling method.

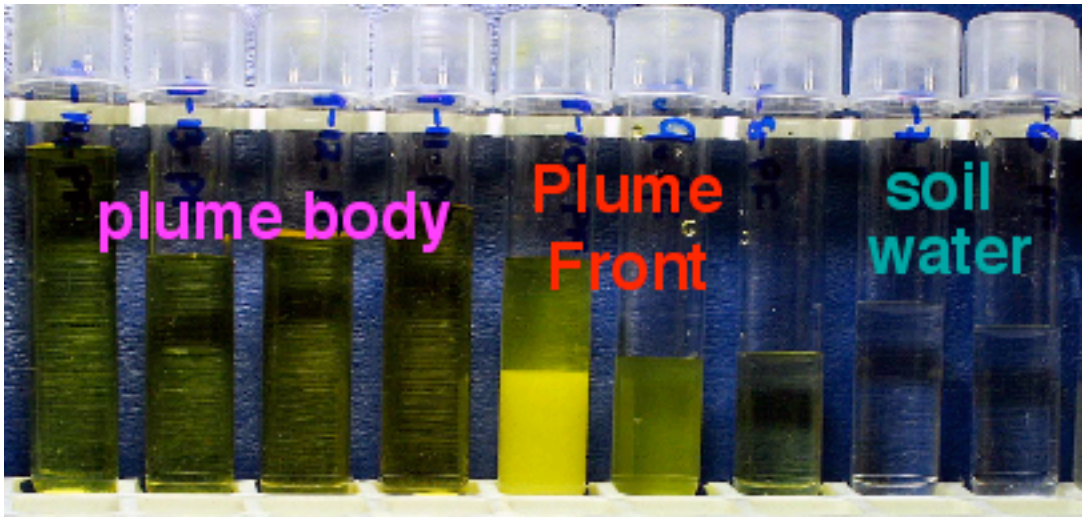

Figure 2. Photograph of a profile of extracted pore solutions from a simulated U plume at the time of initial plume formation. The flow direction is towards the right. Large quantities of U colloids formed at the plume front.

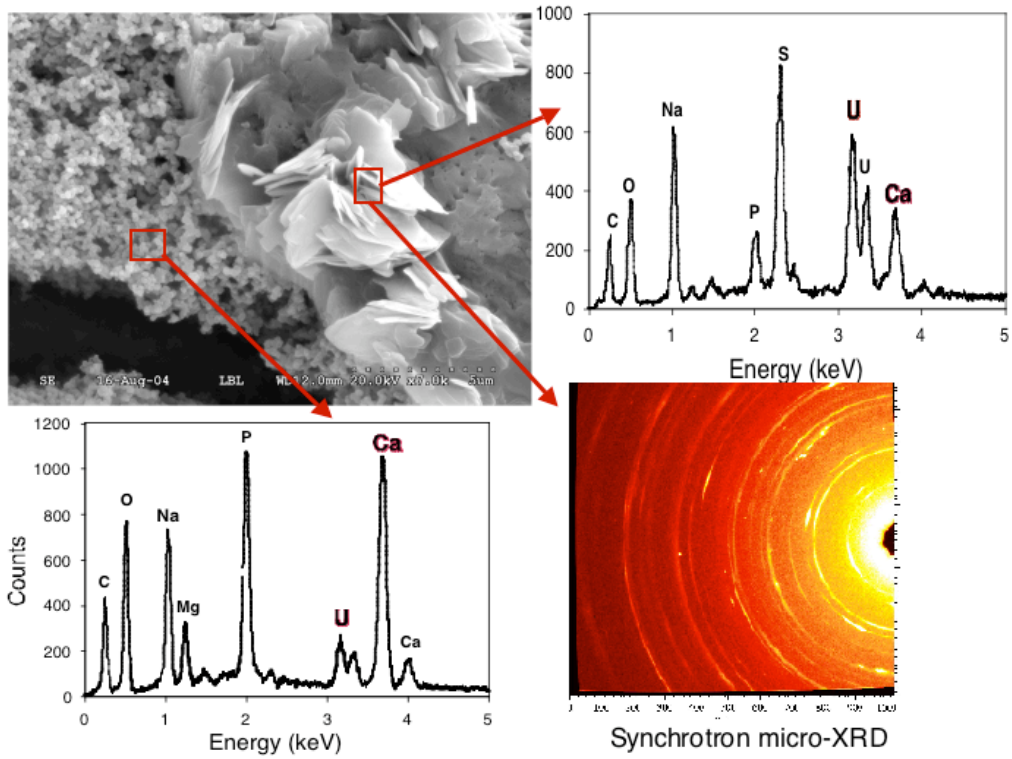

Figure 3. Characterization of the plume front colloids: morphology, chemical composition, and structure. The well crystallized colloidal phase was identified as Cejkaite [$Na_4(UO_2)(CO_3)_3$]

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